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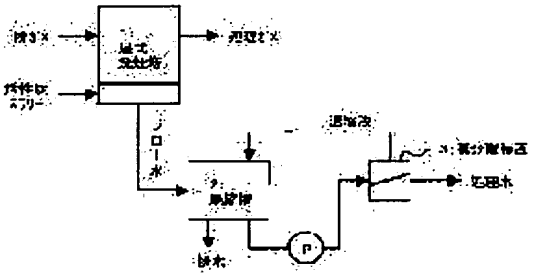
(54) PROCESS AND EQUIPMENT FOR TREATING LIQUID CONTAINING DIOXINS

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a process for treating a liquid containing dioxins, which comprises adding powdery active carbon to the liquid containing dioxins, thereafter subjecting the resulting mixture to solid-liquid separation by a membrane separation means and thereby removing dioxins from the liquid and also, enables reduction in amount of wastewater (a liquid concentrate, i.e., a concentrated slurry of the powdery active carbon containing adsorbed dioxins) discharged from the membrane separation means, advanced removal of dioxins in the dioxin-containing liquid and production of high water quality treated water by securing sufficient time of contact of the dioxin-containing liquid with the powdery active carbon, enhancement of the adsorption of dioxins per unit weight of the powdery active carbon and thereby reduction in required amount of the powdery active carbon.
SOLUTION: This process involves returning a liquid concentrate discharged from a membrane separation means to the inlet side of the membrane separation means. This equipment is provided with a powdery active carbon addition means for adding powdery active carbon to a liquid containing dioxins, the above membrane separation means for subjecting the resulting mixture of the liquid containing dioxins and the added powdery active carbon to solid-liquid separation and a means for returning the liquid concentrate discharged from the membrane separation means to the inlet side of the membrane separation means.



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1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
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CLAIMS

[Claim(s)]
[Claim 1] The art of the dioxin content liquid characterized by returning the concentration liquid of this membrane-separation means to the entrance side of this membrane-separation means in the art of the dioxin content liquid which carries out solid liquid separation using a membrane-separation means after adding powdered activated carbon in dioxin content liquid.
[Claim 2] The art of the dioxin content liquid characterized by having the process which draws out the concentration liquid of this membrane-separation means, the process which carries out coagulation sedimentation separation processing of the drawn-out concentration liquid, and the process which processes the harmful matter in the solid content separated by this coagulation sedimentation separation processing in claim 1.
[Claim 3] The processor of the dioxin content liquid characterized by coming to have a powdered-activated-carbon addition means to add powdered activated carbon in dioxin content liquid, the membrane-separation means which carries out solid liquid separation of the dioxin content liquid with which powdered activated carbon was added, and a means to return the concentration liquid of this membrane-separation means to the entrance side of this membrane-separation means.
[Claim 4] The art of the dioxin content liquid characterized by preparing the reaction vessel which has the unloading and filling pipe of dioxin content liquid, the unloading and filling pipe of the return concentration liquid from this membrane-separation means, and drawing piping of this concentration liquid in the preceding paragraph of said membrane-separation means in claim 3.
[Claim 5] The processor of the dioxin content liquid which is equipment which processes the dioxin content liquid discharged from the wet-scrubber of exhaust gas as raw water in claim 4, and is characterized by forming said powdered-activated-carbon addition means or more [of a wet-scrubber, a raw water tub, a raw water unloading and filling pipe, and a reaction vessel] in any one.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the art and processor of dioxin content liquid from which the technique of removing dioxin from the liquid containing organochlorine compounds (these being hereafter called "dioxin".), such as Pori chlorination-p-dibenzo dioxin (PCDD), polychlorinated dibenzofurans (PCDF), and coplanar one PCB, is started, especially dioxin is removed using powdered activated carbon.
[0002]
[Description of the Prior Art] After carrying out dust removing to an electrostatic precipitator or a bag filter through exhaust gas, such as an incinerator plant, water may be made to contact, water may be made to absorb gas dioxin, and dioxin may be removed out of gas. Dioxin is removed from this underwater one by adding powdered activated carbon, making this powdered activated carbon stick to dioxin in the water which absorbed dioxin, and subsequently separating this powdered activated carbon from this water.
[0003] Although the coagulation sedimentation approach is conventionally used as a solid-liquid-separation means to separate the powdered activated carbon which stuck to these dioxin from said water, when carrying out solid liquid separation of the powdered activated carbon by coagulation sedimentation, some powdered activated carbon may leak to a treated water side, and dioxin may be unable to catch with small quantity.
[0004] By solving this problem and carrying out solid liquid separation of the underwater powdered activated carbon which stuck to dioxin certainly from this water, as an approach of removing dioxin from this water efficiently, previously, these people added powdered activated carbon in dioxin content liquid, and proposed the art of the dioxin content liquid which carries out solid liquid separation using a membrane-separation means after that (JP,11-319809,A). According to this approach, solid liquid separation can be carried out without making the powdered activated carbon which stuck to dioxin completely leak to a treated water side substantially, and it becomes possible to remove dioxin from the water to altitude.
[0005]
[Problem(s) to be Solved by the Invention] According to the approach indicated by JP,11-319809,A, by this approach, although dioxin was removable from dioxin content liquid to altitude, since the concentration liquid which contains the activated carbon which stuck to dioxin from a membrane-separation means was discharged in large quantities, the facility for processing of this concentration liquid was enlarged, and there was a problem that processing cost also soared.
[0006] Moreover, it was difficult to fully secure the contact time of dioxin content liquid and powdered activated carbon, and before dioxin content liquid and powdered activated carbon fully contacted, also when membrane-separation processing may be carried out, for this reason the dioxin amount of adsorption per unit quantity of powdered activated carbon was not fully able to be raised, it was.
[0007] This invention solves the above-mentioned conventional trouble, and after adding powdered activated carbon in dioxin content liquid, in the approach of removing dioxin from dioxin content liquid, it aims at offering the art and processor of dioxin content liquid which can reduce a displacement sharply by carrying out solid liquid separation using a membrane-separation means.
[0008] It aims at offering the art and processor of dioxin content liquid which can raise the dioxin amount of adsorption per [which was added] powdered activated carbon, and can aim at reduction of the initial complement of powdered activated carbon while this invention fully secures the contact time of dioxin content liquid and powdered activated carbon, removes the dioxin in dioxin content liquid to altitude again and obtains

the nature treated water of a flood.
[0009]
[Means for Solving the Problem] After the art of the dioxin content liquid of this invention adds powdered activated carbon in dioxin content liquid, it is characterized by returning the concentration liquid of this membrane-separation means to the entrance side of this membrane-separation means in the art of the dioxin content liquid which carries out solid liquid separation using a membrane-separation means.
[0010] It is characterized by the processor of the dioxin content liquid of this invention coming to have a powdered-activated-carbon addition means to add powdered activated carbon in dioxin content liquid, the membrane-separation means which carries out solid liquid separation of the dioxin content liquid with which powdered activated carbon was added, and a means to return the concentration liquid of this membrane-separation means to the entrance side of this membrane-separation means.
[0011] According to the art and processor of dioxin content liquid of this invention, the concentration volume discharged as wastewater out of a system can be sharply reduced by returning the concentration liquid of a membrane-separation means to the entrance side of a membrane-separation means, and carrying out circulation processing of the concentration liquid. For this reason, while miniaturizing a waste-water-treatment facility, waste-water-treatment cost can be reduced.
[0012] Moreover, the contact time of powdered activated carbon and dioxin content liquid can be lengthened by returning concentration liquid and mixing with raw water, and it becomes possible to fully secure contact time required for making dioxin stick to powdered activated carbon. For this reason, the dioxin amount of adsorption per unit quantity of powdered activated carbon can be raised, much dioxin can be made to be able to adsorb in the small amount of powdered activated carbon, and reduction of the need addition of powdered activated carbon and improvement in quality of treated water can be aimed at.
[0013] In the art of the dioxin content liquid of this invention, the concentration liquid of a membrane-separation means is drawn out and it is desirable to have the process which carries out coagulation sedimentation separation processing of the drawn-out concentration liquid, and processes the harmful matter in the separated solid content.
[0014] Moreover, in the processor of the dioxin content liquid of this invention, it becomes possible to much more fully secure more the contact time of powdered activated carbon and dioxin content liquid by preparing the reaction vessel which has the unloading and filling pipe of dioxin content liquid, the unloading and filling pipe of the return concentration liquid from a membrane-separation means, and drawing piping of concentration liquid in the preceding paragraph of a membrane-separation means.
[0015] Moreover, in the case of the equipment which processes the dioxin content liquid discharged from the wet-scrubber of exhaust gas as raw water, a powdered-activated-carbon addition means can be formed or more [of a wet-scrubber, a raw water tub, a raw water unloading and filling pipe, and a reaction vessel] in any one.
[0016]
[Embodiment of the Invention] The art of the dioxin content liquid of this invention and the gestalt of operation of a processor are explained to a detail below.
[0017] It sets to this invention and the water which washed the cooling water discharged from various incinerators, such as the liquid which contacted the exhaust gas of various kinds of incinerators, such as an incinerator, as dioxin content liquid, and stuck to dioxin, for example, the refuse incinerator equipped with the wet gas washer etc., the leachate of a final disposal site, the smoke scrubbing water of a thermal power station and the solid-state containing dioxin, for example, the fly ash discharged from an incinerator plant, and incinerated ash is illustrated.
[0018] The solubility to the water of dioxin is very low, and the dioxin of ng/L order is dissolving it in the usual water of the case above.
[0019] Especially as powdered activated carbon added to such dioxin content liquid, 200 micrometers or less of maximum grain sizes are 100 micrometers or less, and an about 15-25-micrometer thing is especially desirable [in especially mean particle diameter] in this invention, 10-40 micrometers 50 micrometers or less. In that by which the mean particle diameter of powdered activated carbon exceeds 50 micrometers, since the activated carbon added in dioxin content liquid becomes easy to sediment, dioxin content liquid and activated carbon may fully be unable to contact.
[0020] As for the addition of the powdered activated carbon to dioxin content liquid, it is desirable that they are

300 or more mg/L, and it is desirable that it is especially 500 - 1000 mg/L. If many [if there are few these additions, adsorption treatment of the dioxin cannot fully be carried out, and], it is disadvantageous in respect of cost.

[0021] When adding powdered activated carbon in dioxin content liquid, after adding activated carbon in dioxin content liquid with powder and making liquids (preferably water), such as water and alcohol, or little dioxin content liquid distribute powdered activated carbon, these dispersion liquid may be added in dioxin content liquid. Moreover, a dispersant may be used in order to improve dispersibility of powdered activated carbon. By adding powdered activated carbon as dispersion liquid, homogeneity can be made to distribute powdered activated carbon in dioxin content liquid for a short time, and it is desirable.

[0022] In addition, as powdered activated carbon to add, although a peat system, a coal system, a lignite system, a coconut shell system, etc. are mentioned, the activated carbon of the peat system which has many 20-500A middle holes especially from it being suitable for adsorption of dioxin, and a lignite system is suitable.

[0023] In this invention, although membrane-separation processing is carried out with a membrane-separation means, in order to fully secure the contact time of powdered activated carbon and dioxin content liquid, the dioxin content liquid with which powdered activated carbon was added prepares a reaction vessel in the preceding paragraph of a membrane-separation means if needed, and fully contacts powdered activated carbon and dioxin content liquid within this reaction vessel. That is, if it is necessary to secure the above contact time to some extent, and membrane-separation processing is carried out with a membrane-separation means while this contact time is insufficient in order to make the dioxin in dioxin content liquid fully stick to powdered activated carbon and to remove it, the dioxin in dioxin content liquid cannot be removed to altitude. Contact time required for altitude removal of dioxin is 5 minutes or more preferably 1 minute or more so that clearly also from the result of the below-mentioned example 1 of an experiment. However, when contact time is too long, the processing time becomes long at **, and considering as 5 - 30 minutes is desirable [especially contact time], since it is industrially disadvantageous for 1 to 60 minutes.

[0024] It is desirable to prepare the unloading and filling pipe of the concentration liquid from a membrane-separation means and drawing piping of concentration liquid like the after-mentioned for circulation of the concentration liquid of a membrane-separation means, and to establish the stirring means by an impeller etc. at the reaction vessel prepared in the preceding paragraph of a membrane-separation means in order to secure contact time, in order to raise the contact frequency of powdered activated carbon and dioxin content liquid further.

[0025] In addition, since the contact time of powdered activated carbon is fully secured in the wet-scrubber in many cases when processing the blow water of the wet-scrubber which is performing smoke scrubbing processing by the powdered-activated-carbon slurry by this invention, such a reaction vessel is omissible. However, it is suitable to prepare the thickener tank for return of the concentration liquid of a membrane-separation means (circulation tank) in the preceding paragraph of a membrane-separation means in respect of stabilization of a circulation liquid flow also in this case. Moreover, the raw water tub which stores dioxin content liquid temporarily for stabilization of the amount of dioxin content liquid flows may be prepared in the installation to a membrane-separation means.

[0026] In addition, the addition parts of powdered activated carbon may be any of a raw water tub, a raw water unloading and filling pipe, and a reaction vessel that what is necessary is just the part which the contact time of powdered activated carbon and dioxin content liquid can fully secure. Moreover, you may be the approach of pouring into a wet-scrubber directly like the above-mentioned.

[0027] As a membrane-separation means which carries out membrane-separation processing of the dioxin content liquid which added powdered activated carbon, there is especially no limit and it can use various kinds of membrane modules, such as a spiral mold membrane module, a hollow filament mold membrane module, a flat film mold membrane module, a juxtaductal type membrane module, and an osmosis mold membrane separation device, and a membrane separation device.

[0028] Moreover, as a demarcation membrane, the precision filtration (MF) film and ultrafiltration (UF) film which consist of various materials, such as ceramic film, resin film, and metal precision film, can be used. What cannot stick to dioxin easily like a ceramic as a film material is desirable. Moreover, since hot exhaust gas is washed with the slurry liquid of water or water, and activated carbon, since the dioxin content liquid (smoke scrubbing water) discharged as a result serves as an elevated temperature, what has thermal resistance as a film

material is desirable [especially in the usual case, the thermal resistance of a film material is not needed, but / liquid], when dioxin content liquid is smoke scrubbing water. As a film material from such a point, a ceramic is the most desirable.

[0029] As for especially the aperture of the demarcation membrane to be used, it is desirable that it is about 0.01-0.1 micrometers 0.005-0.2 micrometers. If it is the demarcation membrane of such pore size, the powdered activated carbon in liquid can be made nearly perfect a ** exception. In addition, if pore size is too small, filtration time amount will become long at **. Moreover, when pore size is too large, there is a possibility that activated carbon may leak.

[0030] In this invention, while taking out the permeated water obtained by membrane-separation processing by such membrane-separation means as treated water, concentration liquid is returned to the entrance side of a membrane-separation means, and circulation processing is carried out. Thus, the displacement discharged out of a system can be sharply reduced by carrying out circulation processing of the concentration liquid.

[0031] In this invention, although it changes with water quality, powdered-activated-carbon additions, etc. of the dioxin content liquid to process, by carrying out circulation processing of the concentration liquid in this way, 90 - 99% for the liquid except the solid content in raw water is collected as treated water, and it becomes possible to discharge only the slight concentration liquid of the remainder as wastewater.

[0032] The wastewater drawn out out of the system is the liquid with which the powdered activated carbon which stuck to dioxin was high-condensed, and after carrying out coagulation sedimentation separation processing if needed, as for this wastewater, it is desirable to process harmful matter in the separated solid content. As a processing means of this harmful matter, in many cases, incineration disposal of solid content is performed, but solid content may be heated and decholorinated or decomposition drugs or a microorganism may decompose dioxin. Moreover, when heavy metal is further contained in solid content, processing which fixes this with drugs may be performed. Moreover, the wastewater drawn out out of the system may be reused as activated carbon for dioxin removal, such as a wet-scrubber, after performing suitable processing.

[0033] In addition, preliminary solid-liquid-separation processing, such as natural sedimentation processing, centrifugal separation processing, coagulative separation, and floatation, may be performed for dioxin content liquid after adding powdered activated carbon and making it fully contact in advance of membrane separation by the above-mentioned membrane-separation means. Moreover, in order to raise further the contacting efficiency of powdered activated carbon and dioxin content liquid, a line mixer etc. may be formed in migration piping of liquid. Moreover, dioxin content liquid may cool the addition front stirrup of powdered activated carbon if needed after addition.

[0034]

[Example] The example of an experiment, an example, and the example of a comparison are given to below, and this invention is more concretely explained to it.

[0035] The experiment which investigates the relation between the contact time of example of experiment 1 dioxin content liquid and powdered activated carbon and the dioxin removal effectiveness was conducted.

[0036] The blow water (SS:60 mg/L, dioxin concentration:1.2 ng-TEQ/L) of the wet-scrubber of an incinerator plant is introduced into a reaction vessel. Peat system powdered activated carbon (main pore size of 20-500A, mean particle diameter of 20 micrometers) is added at a rate of 500 mg/L. 0.5 minutes, After stirring, respectively for 1 minute, 5 minutes, 10 minutes, 30 minutes, 60 minutes, and 120 minutes, membrane-separation processing was carried out by 2Oaluminum3 film production of 0.05 micrometers of apertures, the dioxin concentration of treated water (permeated water) was measured, and the result was shown in drawing 3 .

[0037] Drawing 3 shows that the contact time for 5 minutes or more is preferably required 1 minute or more, in order to fully carry out adsorption treatment of the dioxin.

[0038] With the equipment shown in example 1 drawing 1 , dioxin content liquid was processed according to this invention.

[0039] With this equipment, the blow water of the wet-scrubber 1 which is carrying out smoke scrubbing of the exhaust gas of an incinerator plant by the powdered-activated-carbon slurry was used as raw water, through the thickener tank 2, the membrane separation device 3 was supplied with Pump P, solid liquid separation was carried out, and it took out out of the system by having used permeated water as treated water, and circulated through concentration liquid to the thickener tank 2.

[0040] In addition, the addition is about 90% in SS of the blow water of a wet-scrubber 1 (about 500 mg/L),

using peat system activated carbon (20-500A of main pore size, 20 micrometers of mean diameters) as powdered activated carbon.
[0041] Moreover, membrane-separation processing conditions were carried out as follows, using 2Oaluminum3 film production of 0.05 micrometers of apertures as a demarcation membrane of a membrane separation device.
[Membrane-separation processing conditions]
Raw water inflow : The amount of 310 L/hr treated water fetch : 300 L/hr concentration liquid circulating load : The amount of concentration liquid drawing from a 3000 L/hr thickener tank: From the raw water (wet-scrubber blow water) of 10 L/hr consequently SS:543 mg/L, and dioxin concentration:79 ng-TEQ/L, the treated water of dioxin concentration:0.0045 ng-TEQ/L was obtained, and the high dioxin removal effectiveness was attained. Moreover, when the water in a thickener tank 2 was analyzed, SS concentration is 7840 mg/L and was condensed 14.4 times compared with raw water.
[0042] In this example 1, although the configuration from which, especially as for the thickener tank 2, the residence time is secured since [that powdered activated carbon and dioxin content liquid are enough] time amount contact is carried out is not carried out into the wet-scrubber 1, the function as a reaction vessel may be given to this thickener tank 2.
[0043] Although the dioxin concentration of the obtained treated water was 0.0030 ng-TEQ/L and the dioxin removal effectiveness was good when similarly processed except having discharged and operated out of the system in example of comparison 1 example 1, without returning the concentration liquid of a membrane separation device to a thickener tank, it was 180 times [in the case of an example 1] the amount of wastewater (concentration liquid) of this discharged out of a system.
[0044] It turns out that a displacement can be reduced sharply, without changing most of the removal effectiveness of dioxin from the result of an example 1 and the example 1 of a comparison by carrying out circulation processing of the concentration liquid of a membrane separation device.
[0045] With the equipment shown in example 2 drawing 2 , dioxin content liquid was processed according to this invention.
[0046] With this equipment, the blow water (SS:60 mg/L, dioxin concentration:1.5 ng-TEQ/L) of the wet-scrubber of an incinerator plant is introduced into a reaction vessel 4. After adding and making peat system powdered activated carbon (main pore size of 50-200A, mean particle diameter of 20 micrometers) pile up at a rate of 500 mg/L, with Pump P Solid liquid separation was supplied and carried out to the membrane separation device 5 equipped with 2Oaluminum3 film production of 0.05 micrometers of apertures, and it circulated through drawing and concentration liquid to the reaction vessel 4 out of the system by using permeated water as treated water.
[0047] In addition, the residence time in a reaction vessel 4 operated by [as it having been 1 hour], and carried out membrane-separation processing conditions as follows.
[Membrane-separation processing conditions]
Raw water inflow : The amount of 200 L/hr treated water fetch : 190 L/hr concentration liquid circulating load : The amount of concentration liquid drawing from a 2000 L/hr reaction vessel: When the dioxin concentration of the treated water obtained 10 L/hr was measured, dioxin was not detected out of treated water.
[0048] In example of comparison 2 example 2, a reaction vessel was not prepared, but it carried out similarly except having poured in so that it might become an activated carbon addition equivalent to an example 2 about a powdered-activated-carbon slurry in water supply Rhine before [1m] a membrane separation device.
[0049] Consequently, the dioxin concentration of the obtained treated water is 0.3 ng-TEQ/L, and was not able to acquire sufficient dioxin removal effectiveness.
[0050] By preparing a reaction vessel in the preceding paragraph of a membrane separation device, and securing the contact time of dioxin content liquid and powdered activated carbon from the result of an example 2 and the example 2 of a comparison shows that dioxin is removable to altitude.
[0051]
[Effect of the Invention] Since the wastewater (concentration liquid) discharged from a membrane-separation means can be reduced sharply in according to this invention the above passage removing dioxin from dioxin content liquid by carrying out solid liquid separation using a membrane-separation means after adding powdered activated carbon in dioxin content liquid, miniaturization of a waste-water-treatment facility and reduction of waste-water-treatment cost can be aimed at.

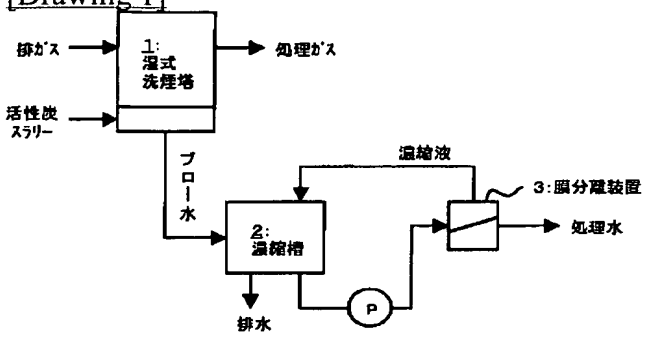
[0052] Moreover, while fully securing the contact time of dioxin content liquid and powdered activated carbon, removing the dioxin in dioxin content liquid to altitude and obtaining the nature treated water of a flood, the dioxin amount of adsorption per [which was added] powdered activated carbon can be raised, and reduction of the initial complement of powdered activated carbon can be aimed at.

[Translation done.]

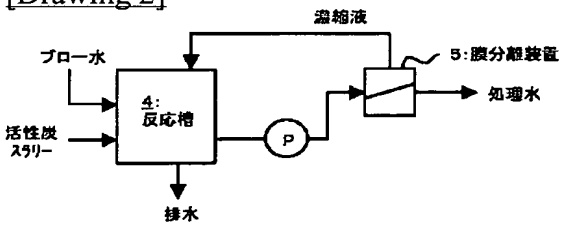
* NOTICES *

DRAWINGS

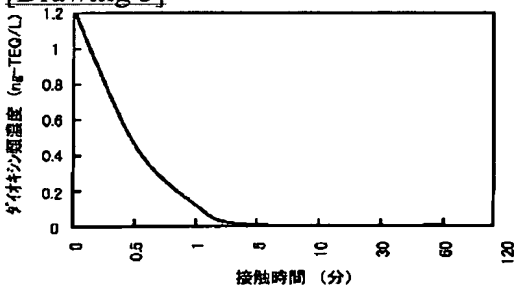
[Drawing 1]



[Drawing 2]



[Drawing 3]



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PROCESS AND EQUIPMENT FOR TREATING LIQUID CONTAINING DIOXINS

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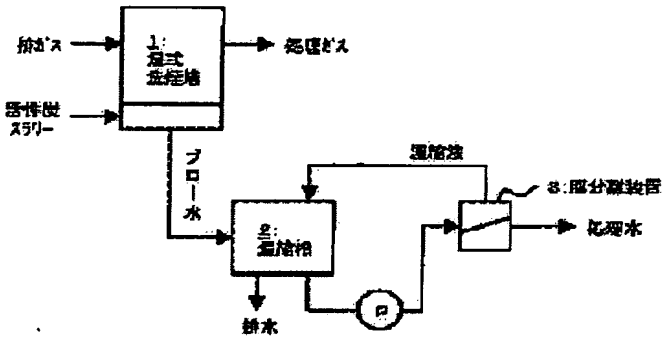
Abstract of **JP2001232356**

PROBLEM TO BE SOLVED: To provide a process for treating a liquid containing dioxins, which comprises adding powdery active carbon to the liquid containing dioxins, thereafter subjecting the resulting mixture to solid-liquid separation by a membrane separation means and thereby removing dioxins from the liquid and also, enables reduction in amount of wastewater (a liquid concentrate, i.e., a concentrated slurry of the powdery active carbon containing adsorbed dioxins) discharged from the membrane separation means, advanced removal of dioxins in the dioxin-containing liquid and production of high water quality treated water by securing sufficient time of contact of the dioxin-containing liquid with the powdery active carbon, enhancement of the adsorption of dioxins per unit weight of the powdery active carbon and thereby reduction in required amount of the powdery active carbon. SOLUTION: This process involves returning a liquid concentrate discharged from a membrane separation means to the inlet side of the membrane separation means. This equipment is provided with a powdery active carbon addition means for adding powdery active carbon to a liquid containing dioxins, the above membrane separation means for subjecting the resulting mixture of the liquid containing dioxins and the added powdery active carbon to solid-liquid separation and a means for returning the liquid concentrate discharged from the membrane separation means to the inlet side of the membrane separation means.



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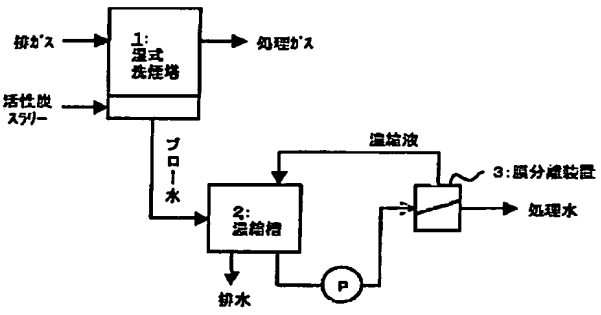
最終頁に続く

(54)【発明の名称】　ダイオキシン類含有液の処理方法及び処理装置

(57)【要約】
【課題】　ダイオキシン類含有液に粉末活性炭を添加した後膜分離手段を用いて固液分離することによりダイオキシン類含有液からダイオキシン類を除去する方法において、膜分離手段からの排水量を低減する。また、ダイオキシン類含有液と粉末活性炭との接触時間を十分に確保してダイオキシン類含有液中のダイオキシン類を高度に除去して高水質処理水を得ると共に、添加した粉末活性炭当たりのダイオキシン類吸着量を高めて粉末活性炭の必要量の低減を図る。
【解決手段】　膜分離手段の濃縮液を膜分離手段の入口側へ返送するダイオキシン類含有液の処理方法。ダイオキシン類含有液に粉末活性炭を添加する粉末活性炭添加手段と、粉末活性炭が添加されたダイオキシン類含有液を固液分離する膜分離手段と、膜分離手段の濃縮液を膜分離手段の入口側に返送する手段とを備えてなるダイオキシン類含有液の処理装置。



【特許請求の範囲】
【請求項１】　ダイオキシン類含有液に粉末活性炭を添加した後、膜分離手段を用いて固液分離するダイオキシン類含有液の処理方法において、
該膜分離手段の濃縮液を該膜分離手段の入口側へ返送することを特徴とするダイオキシン類含有液の処理方法。
【請求項２】　請求項１において、該膜分離手段の濃縮液を引き抜く工程と、
引き抜いた濃縮液を凝集沈殿分離処理する工程と、
該凝集沈殿分離処理で分離された固形分中の有害物質を処理する工程とを備えることを特徴とするダイオキシン類含有液の処理方法。
【請求項３】　ダイオキシン類含有液に粉末活性炭を添加する粉末活性炭添加手段と、
粉末活性炭が添加されたダイオキシン類含有液を固液分離する膜分離手段と、
該膜分離手段の濃縮液を該膜分離手段の入口側に返送する手段とを備えてなることを特徴とするダイオキシン類含有液の処理装置。
【請求項４】　請求項３において、前記膜分離手段の前段に、ダイオキシン類含有液の受入配管と、該膜分離手段からの返送濃縮液の受入配管と、該濃縮液の引き抜き配管とを有する反応槽が設けられていることを特徴とするダイオキシン類含有液の処理方法。
【請求項５】　請求項４において、排ガスの湿式洗煙塔から排出されるダイオキシン類含有液を原水として処理する装置であって、前記粉末活性炭添加手段が湿式洗煙塔、原水槽、原水受入配管及び反応槽のいずれか１以上に設けられていることを特徴とするダイオキシン類含有液の処理装置。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、ポリ塩化－ｐ－ジベンゾダイオキシン類（ＰＣＤＤ）やポリ塩化ジベンゾフラン類（ＰＣＤＦ）、コプラナーＰＣＢ等の有機塩素化合物（以下、これらを「ダイオキシン類」と称す。）を含有した液からダイオキシン類を除去する技術に係り、特に粉末活性炭を用いてダイオキシン類を除去するダイオキシン類含有液の処理方法及び処理装置に関する。
【０００２】
【従来の技術】ごみ焼却場等の排ガスを、電気集塵機やバグフィルタに通して除塵した後、水と接触させてガス状のダイオキシン類を水に吸収させてガス中からダイオキシン類を除去することがある。ダイオキシン類を吸収した水は、粉末活性炭が添加され、ダイオキシン類を該粉末活性炭に吸着させ、次いでこの粉末活性炭を該水から分離することにより、該水中からダイオキシン類が除去される。
【０００３】従来、このダイオキシン類を吸着した粉末活性炭を前記水から分離する固液分離手段としては凝集沈殿処理法が用いられているが、凝集沈殿により粉末活性炭を固液分離する場合、若干の粉末活性炭が処理水側にリークし、ダイオキシン類が少量ながら捕捉できないことがある。
【０００４】この問題を解決し、ダイオキシン類を吸着した水中の粉末活性炭を該水から確実に固液分離することにより、該水からダイオキシン類を効率的に除去する方法として、本出願人は先に、ダイオキシン類含有液に粉末活性炭を添加し、その後膜分離手段を用いて固液分離するダイオキシン類含有液の処理方法を提案した（特開平１１－３１９８０９号公報）。この方法によれば、ダイオキシン類を吸着した粉末活性炭を処理水側に実質的に全くリークさせることなく固液分離することができ、水中からダイオキシン類を高度に除去することが可能となる。
【０００５】
【発明が解決しようとする課題】特開平１１－３１９８０９号公報に記載される方法によれば、ダイオキシン類含有液からダイオキシン類を高度に除去することができるが、この方法では、膜分離手段から、ダイオキシン類を吸着した活性炭を含む濃縮液が大量に排出されるため、この濃縮液の処理のための設備が大型化し、処理コストも高騰するという問題があった。
【０００６】また、ダイオキシン類含有液と粉末活性炭との接触時間を十分に確保することが難しく、ダイオキシン類含有液と粉末活性炭とが十分に接触しないうちに膜分離処理されてしまう場合があり、このために、粉末活性炭の単位量当たりのダイオキシン類吸着量を十分に高めることができない場合もあった。
【０００７】本発明は上記従来の問題点を解決し、ダイオキシン類含有液に粉末活性炭を添加した後膜分離手段を用いて固液分離することによりダイオキシン類含有液からダイオキシン類を除去する方法において、排水量を大幅に低減することができるダイオキシン類含有液の処理方法及び処理装置を提供することを目的とする。
【０００８】本発明はまた、ダイオキシン類含有液と粉末活性炭との接触時間を十分に確保してダイオキシン類含有液中のダイオキシン類を高度に除去して高水質処理水を得ると共に、添加した粉末活性炭当たりのダイオキシン類吸着量を高めて粉末活性炭の必要量の低減を図ることができるダイオキシン類含有液の処理方法及び処理装置を提供することを目的とする。
【０００９】
【課題を解決するための手段】本発明のダイオキシン類含有液の処理方法は、ダイオキシン類含有液に粉末活性炭を添加した後、膜分離手段を用いて固液分離するダイオキシン類含有液の処理方法において、該膜分離手段の濃縮液を該膜分離手段の入口側へ返送することを特徴とする。

【００１０】本発明のダイオキシン類含有液の処理装置は、ダイオキシン類含有液に粉末活性炭を添加する粉末活性炭添加手段と、粉末活性炭が添加されたダイオキシン類含有液を固液分離する膜分離手段と、該膜分離手段の濃縮液を該膜分離手段の入口側に返送する手段とを備えてなることを特徴とする。

【００１１】本発明のダイオキシン類含有液の処理方法及び処理装置によれば、膜分離手段の濃縮液を膜分離手段の入口側に返送して濃縮液を循環処理することにより、系外へ排水として排出する濃縮液量を大幅に低減することができる。このため、排水処理設備を小型化すると共に、排水処理コストを低減することができる。

【００１２】また、濃縮液を返送して原水と混合することで、粉末活性炭とダイオキシン類含有液との接触時間を長くすることができ、ダイオキシン類を粉末活性炭に吸着させるに必要な接触時間を十分に確保することが可能となる。このため、粉末活性炭の単位量当たりのダイオキシン類吸着量を高め、少ない粉末活性炭量で多くのダイオキシン類を吸着させて粉末活性炭の必要添加量の低減、処理水水質の向上を図ることができる。

【００１３】本発明のダイオキシン類含有液の処理方法では、膜分離手段の濃縮液を引き抜き、引き抜いた濃縮液を凝集沈殿分離処理し、分離された固形分中の有害物質を処理する工程を備えることが好ましい。

【００１４】また、本発明のダイオキシン類含有液の処理装置においては、膜分離手段の前段に、ダイオキシン類含有液の受入配管と、膜分離手段からの返送濃縮液の受入配管と、濃縮液の引き抜き配管とを有する反応槽を設けることにより、粉末活性炭とダイオキシン類含有液との接触時間をより一層十分に確保することが可能となる。

【００１５】また、排ガスの湿式洗煙塔から排出されるダイオキシン類含有液を原水として処理する装置の場合、粉末活性炭添加手段は、湿式洗煙塔、原水槽、原水受入配管及び反応槽のいずれか１以上に設けることができる。

【００１６】

【発明の実施の形態】以下に本発明のダイオキシン類含有液の処理方法及び処理装置の実施の形態を詳細に説明する。

【００１７】本発明において、ダイオキシン類含有液としては、ゴミ焼却炉等の各種の焼却炉の排ガスと接触してダイオキシン類を吸着した液、例えば、湿式洗煙装置を備えたごみ焼却炉等の各種焼却炉から排出される冷却水や、最終処分場の浸出水、火力発電の洗煙排水、ダイオキシン類を含有する固体、例えばごみ焼却場から排出される飛灰や焼却灰を洗浄した水などが例示される。

【００１８】ダイオキシン類の水に対する溶解度はきわめて低く、通常の場合上記の水にはｎｇ／Ｌオーダーのダイオキシン類が溶解している。

【００１９】本発明において、このようなダイオキシン類含有液に対し添加する粉末活性炭としては、最大粒径が２００μｍ以下特に１００μｍ以下であり、平均粒径では５０μｍ以下、特に１０～４０μｍ、とりわけ１５～２５μｍ程度のものが好ましい。粉末活性炭の平均粒径が５０μｍを超えるものでは、ダイオキシン類含有液に添加した活性炭が沈降しやすくなるため、ダイオキシン類含有液と活性炭とが十分に接触できない可能性がある。

【００２０】ダイオキシン類含有液に対する粉末活性炭の添加量は、３００ｍｇ／Ｌ以上であることが好ましく、特に５００～１０００ｍｇ／Ｌであることが好ましい。この添加量が少ないとダイオキシン類を十分に吸着除去することができず、多いとコスト面で不利である。

【００２１】粉末活性炭をダイオキシン類含有液に添加する場合、粉末のまま活性炭をダイオキシン類含有液に添加しても良く、粉末活性炭を水、アルコールなどの液体（好ましくは水）、あるいは少量のダイオキシン類含有液に分散させた後、この分散液をダイオキシン類含有液に添加しても良い。また、粉末活性炭の分散性を良くするために分散剤を用いても良い。粉末活性炭を分散液として添加することにより、ダイオキシン類含有液中に粉末活性炭を短時間で均一に分散させることができ、好ましい。

【００２２】なお、添加する粉末活性炭としては、ピート系、石炭系、亜炭系、ヤシガラ系等が挙げられるが、ダイオキシン類の吸着に適していることから、特に２０～５００Åの中間孔を多く有するピート系、亜炭系の活性炭が好適である。

【００２３】粉末活性炭が添加されたダイオキシン類含有液は、膜分離手段で膜分離処理されるが、本発明においては、粉末活性炭とダイオキシン類含有液との接触時間を十分に確保するために、必要に応じて膜分離手段の前段に反応槽を設け、この反応槽内で粉末活性炭とダイオキシン類含有液とを十分に接触させる。即ち、ダイオキシン類含有液中のダイオキシン類を粉末活性炭に十分に吸着させて除去するためには、ある程度以上の接触時間を確保する必要があり、この接触時間が不十分なうちに膜分離手段で膜分離処理すると、ダイオキシン類含有液中のダイオキシン類を高度に除去し得ない。ダイオキシン類の高度除去に必要な接触時間は、後述の実験例１の結果からも明らかなように、１分以上、好ましくは５分以上である。ただし、接触時間が過度に長いと処理時間が徒に長くなって工業的に不利であるため、接触時間は１～６０分、特に５～３０分とするのが好ましい。

【００２４】接触時間を確保するために膜分離手段の前段に設ける反応槽には、後述の如く、膜分離手段の濃縮液の循環のために、膜分離手段からの濃縮液の受入配管と濃縮液の引き抜き配管を設け、更に、粉末活性炭とダイオキシン類含有液との接触頻度を高めるために、撹拌

羽根等による撹拌手段等を設けるのが好ましい。

【００２５】なお、本発明により、粉末活性炭スラリーで洗煙処理を行っている湿式洗煙塔のブロー水を処理する場合においては、多くの場合、湿式洗煙塔内において、粉末活性炭の接触時間が十分に確保されていることから、このような反応槽を省略することができる。ただし、この場合においても、膜分離手段の濃縮液の返送のための濃縮槽（循環槽）を膜分離手段の前段に設けるのが、循環液流の安定化の面で好適である。また、膜分離手段への導入に当たり、ダイオキシン類含有液流量の安定化のために、ダイオキシン類含有液を一時的に貯留する原水槽を設けても良い。

【００２６】なお、粉末活性炭の添加箇所は、粉末活性炭とダイオキシン類含有液との接触時間が十分に確保できるような箇所であれば良く、原水槽、原水受入配管、反応槽のいずれであっても良い。また、前述の如く、湿式洗煙塔に直接注入する方法であっても良い。

【００２７】粉末活性炭を添加したダイオキシン類含有液を膜分離処理する膜分離手段としては特に制限はなく、スパイラル型膜モジュール、中空糸型膜モジュール、平膜型膜モジュール、管型膜モジュール、浸透型膜分離装置など各種の膜モジュール、膜分離装置を用いることができる。

【００２８】また、分離膜としては、セラミック膜、樹脂膜、金属製精密膜など各種素材よりなる精密沪過（ＭＦ）膜や限外沪過（ＵＦ）膜を用いることができる。膜素材としては、セラミックのようにダイオキシン類を吸着し難いものが好ましい。また、膜素材の耐熱性は通常の場合特に必要とされないが、ダイオキシン類含有液が洗煙排水の場合は、高温の排ガスを水又は水と活性炭のスラリー液により洗うことから、結果として排出されるダイオキシン類含有液（洗煙排水）は高温となるため、膜素材としては耐熱性を持っているものが望ましい。このような点から、膜素材としてはセラミックが最も好ましい。

【００２９】用いる分離膜の孔径は０．００５～０．２μm、特に０．０１～０．１μm程度であることが好ましい。このような細孔径の分離膜であれば、液中の粉末活性炭をほぼ完全に沪別することができる。なお、細孔径が過度に小さいと、沪過時間が徒に長くなる。また、細孔径が過度に大きいと、活性炭がリークするおそれがある。

【００３０】本発明においては、このような膜分離手段による膜分離処理により得られた透過水を処理水として取り出す一方で、濃縮液を膜分離手段の入口側へ返送して循環処理する。このように、濃縮液を循環処理することにより、系外へ排出する排水量を大幅に低減することができる。

【００３１】本発明においては、処理するダイオキシン類含有液の水質や粉末活性炭添加量等によっても異なるが、このように濃縮液を循環処理することにより、原水中の固形分を除く液分の９０～９９％を処理水として回収し、残部のわずかな濃縮液のみを排水として排出することが可能となる。

【００３２】系外へ引き抜かれた排水は、ダイオキシン類を吸着した粉末活性炭が高濃縮された液であり、この排水は、必要に応じて凝集沈殿分離処理した後、分離された固形分中の有害物質の処理を行うのが好ましい。この有害物質の処理手段としては、多くの場合、固形分の焼却処分が行われるが、その他、固形分を加熱して脱塩素処理したり、分解薬剤又は微生物によりダイオキシン類を分解したりしても良い。また、固形分中に更に重金属類が含まれている場合には、薬剤によりこれを固定化する処理を施しても良い。また、系外へ引き抜いた排水は、適当な処理を施した後、湿式洗煙塔等のダイオキシン類除去用活性炭として再利用しても良い。

【００３３】なお、上記膜分離手段による膜分離に先立ち、粉末活性炭を添加して十分に接触させた後のダイオキシン類含有液を自然沈降分離処理、遠心分離処理、凝集分離、浮上分離など予備的な固液分離処理を行っても良い。また、粉末活性炭とダイオキシン類含有液との接触効率をより一層高めるために、液の移送配管にラインミキサ等を設けても良い。また、ダイオキシン類含有液は粉末活性炭の添加前又は添加後に必要に応じて冷却しても良い。

【００３４】

【実施例】以下に実験例、実施例及び比較例を挙げて本発明をより具体的に説明する。

【００３５】実験例１

ダイオキシン類含有液と粉末活性炭との接触時間とダイオキシン類除去効果との関係を調べる実験を行った。

【００３６】ごみ焼却場の湿式洗煙塔のブロー水（ＳＳ：６０ｍｇ／Ｌ，ダイオキシン類濃度：１．２ｎｇ－ＴＥＱ／Ｌ）を反応槽に導入し、ピート系粉末活性炭（中心細孔径２０～５００Å，平均粒径２０μｍ）を５００ｍｇ／Ｌの割合で添加して０．５分、１分、５分、１０分、３０分、６０分、１２０分間それぞれ撹拌した後、孔径０．０５μｍのAl_2O_3製膜で膜分離処理し、処理水（透過水）のダイオキシン類濃度を測定し、結果を図３に示した。

【００３７】図３より、ダイオキシン類を十分に吸着除去するためには、１分以上、好ましくは５分以上の接触時間が必要であることがわかる。

【００３８】実施例１

図１に示す装置で、本発明に従ってダイオキシン類含有液の処理を行った。

【００３９】この装置では、ごみ焼却場の排ガスを粉末活性炭スラリーで洗煙している湿式洗煙塔１のブロー水を原水とし、濃縮槽２を経てポンプＰにより膜分離装置３に供給して固液分離し、透過水を処理水として系外へ

取り出し、濃縮液は濃縮槽２に循環した。

【００４０】なお、粉末活性炭としては、ピート系活性炭（中心細孔径２０～５００Å，平均粒径２０μｍ）を用い、その添加量は湿式洗煙塔１のブロー水のＳＳ中の約９０％程度（約５００ｍｇ／Ｌ）である。

【００４１】また、膜分離装置の分離膜としては、孔径０．０５μｍのAl_2O_3製膜を用い、膜分離処理条件は以下の通りとした。

〔膜分離処理条件〕

原水流入量	：３１０Ｌ／ｈｒ
処理水取出量	：３００Ｌ／ｈｒ
濃縮液循環量	：３０００Ｌ／ｈｒ
濃縮槽からの濃縮液引き抜き量	：１０Ｌ／ｈｒ

その結果、ＳＳ：５４３ｍｇ／Ｌ，ダイオキシン類濃度：７９ｎｇ－ＴＥＱ／Ｌの原水（湿式洗煙塔ブロー水）から、ダイオキシン類濃度：０．００４５ｎｇ－ＴＥＱ／Ｌの処理水が得られ、高いダイオキシン類除去効果が達成された。また、濃縮槽２内の水を分析したところ、ＳＳ濃度は７８４０ｍｇ／Ｌであり、原水と比べて１４．４倍に濃縮されていた。

【００４２】この実施例１においては、湿式洗煙塔１内において粉末活性炭とダイオキシン類含有液とが十分な時間接触しているため、濃縮槽２は、特に滞留時間が確保される構成とはされていないが、この濃縮槽２に反応槽としての機能を持たせても良い。

【００４３】比較例１

実施例１において、膜分離装置の濃縮液を濃縮槽に返送せずに系外に排出して運転したこと以外は、同様にして処理を行ったところ、得られた処理水のダイオキシン類濃度は０．００３０ｎｇ－ＴＥＱ／Ｌで、ダイオキシン類除去効果は良好であったが、系外へ排出される排水（濃縮液）量は実施例１の場合の１８０倍であった。

【００４４】実施例１及び比較例１の結果から、膜分離装置の濃縮液を循環処理することにより、ダイオキシン類の除去効果を殆ど変えることなく、排水量を大幅に低減できることがわかる。

【００４５】実施例２

図２に示す装置で、本発明に従ってダイオキシン類含有液の処理を行った。

【００４６】この装置では、ごみ焼却場の湿式洗煙塔のブロー水（ＳＳ：６０ｍｇ／Ｌ，ダイオキシン類濃度：１．５ｎｇ－ＴＥＱ／Ｌ）を反応槽４に導入し、ピート系粉末活性炭（中心細孔径５０～２００Å，平均粒径２０μｍ）を５００ｍｇ／Ｌの割合で添加して滞留させた後、ポンプＰにより、孔径０．０５μｍのAl_2O_3製膜を装着した膜分離装置５に供給して固液分離し、透過水を処理水として系外へ取出し、濃縮液は反応槽４に循環した。

【００４７】なお、反応槽４における滞留時間は１時間となるようにして運転を行い、膜分離処理条件は以下の通りとした。

〔膜分離処理条件〕

原水流入量	：２００Ｌ／ｈｒ
処理水取出量	：１９０Ｌ／ｈｒ
濃縮液循環量	：２０００Ｌ／ｈｒ
反応槽からの濃縮液引き抜き量	：１０Ｌ／ｈｒ

得られた処理水のダイオキシン類濃度を測定したところ、処理水中からダイオキシン類は検出されなかった。

【００４８】比較例２

実施例２において、反応槽を設けず、膜分離装置の１ｍ手前の送水ラインに粉末活性炭スラリーを実施例２と同等の活性炭添加量となるように、注入したこと以外は同様にして行った。

【００４９】その結果、得られた処理水のダイオキシン類濃度は０．３ｎｇ－ＴＥＱ／Ｌで、十分なダイオキシン類除去効果を得ることはできなかった。

【００５０】実施例２及び比較例２の結果から、膜分離装置の前段に反応槽を設けてダイオキシン類含有液と粉末活性炭との接触時間を確保することにより、ダイオキシン類を高度に除去することができることがわかる。

【００５１】

【発明の効果】以上の通り、本発明によれば、ダイオキシン類含有液に粉末活性炭を添加した後膜分離手段を用いて固液分離することによりダイオキシン類含有液からダイオキシン類を除去するに当たり、膜分離手段から排出される排水（濃縮液）を大幅に低減することができるため、排水処理設備の小型化、排水処理コストの低減を図ることができる。

【００５２】また、ダイオキシン類含有液と粉末活性炭との接触時間を十分に確保してダイオキシン類含有液中のダイオキシン類を高度に除去して高水質処理水を得ると共に、添加した粉末活性炭当たりのダイオキシン類吸着量を高めて粉末活性炭の必要量の低減を図ることができる。

【図面の簡単な説明】

【図１】実施例１における処理装置を示す系統図である。

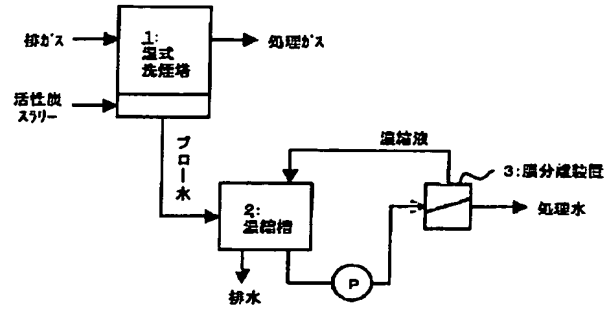
【図２】実施例２における処理装置を示す系統図である。

【図３】実験例１で求めた接触時間と処理水のダイオキシン類濃度との関係を示すグラフである。

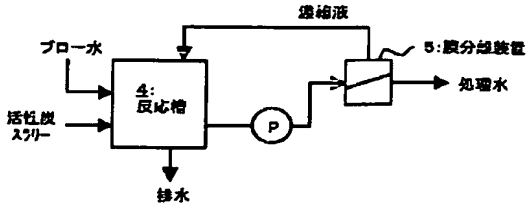
【符号の説明】

１　湿式洗煙塔
２　濃縮槽
３，５　膜分離装置
４　反応槽

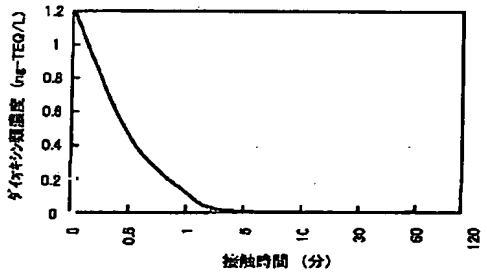
【図1】



【図2】



【図3】



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